Prospects and Challenges of Solid Electrolytes in Lithium Rechargeable Batteries

William West, Jay Whitacre*, Keith Billings, Simon Jones, Erik Brandon and Kumar Bugga

Jet Propulsion Laboratory,
California Institute of Technology,
Pasadena, CA 91109

* Carnegie Mellon University

2019 MRS Spring Meeting & Exhibit
April 22-26, 2019
Phoenix, AZ

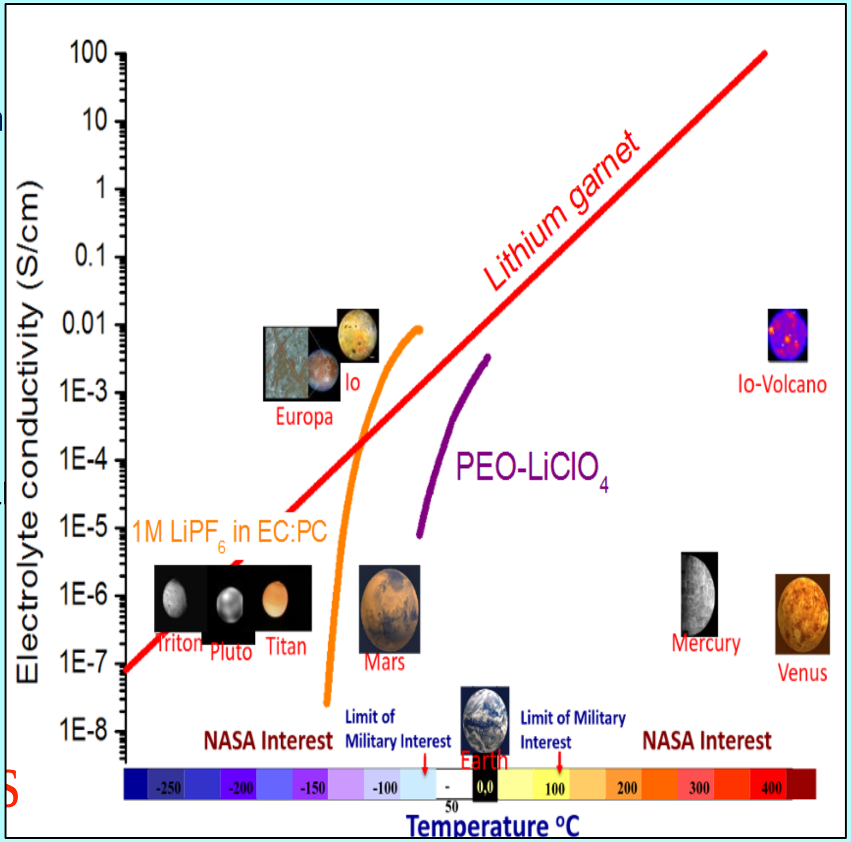
Batteries for Space Applications

Category	Mission	Battery Performance Drivers	Chemistry
Outer Planets: Ocean Worlds (Europa, Titan, Enceladus)	Orbital Missions	Long Cycle life (at partial depth of discharge)	Li-ion
	Surface Missions	Primary or rechargeable - high specific energy, long calendar life	Li-CF_x or Li-ion,
	Sample Return Missions	Primary Long calendar life High specific energy and energy density	Li-CF_X and Li-$SOCl_2$,
Outer Planets: ICE Giants (Neptune, Uranus)	Orbiters	Long Cycle life (at partial depth of discharge	Li-ion
	Probes	Primary - high specific energy, long calendar life	Li-CF_X and Li-$SOCl_2$,
Inner Planets: Venus	Orbital	Long Cycle life (at partial depth of discharge	Li-ion
	Aerial	High Temperature, high specific energy and good cycle life	Na-MCl_2
	Surface	Primary High Temperature, high specific energy	Li-FeS_2
Mars	Sample Return Missions	Primary Long calendar life High specific energy and energy density	Li-CF_X and Li-$SOCl_2$,
	Orbital Missions	Long Cycle life (at partial depth of discharge)	Li-ion
	Aerial Missions	High specific energy, energy density and high power density	Li-ion
	Surface Missions	High specific energy, energy density and low temperature performance	Li-ion
Small Bodies : Multi-asteroid rendezvous or flyby mission	Sample Return Missions	Primary Long calendar life High specific energy and energy density	Li-SO_2 Li-$SOCl_2$,
	Surface missions	Primary or rechargeable - high specific energy,	Li-ion or Li-S
Planetary Cube Sat/ Small Spacecraft		High specific energy, energy density and low temperature performance	Li-ion or Li-S
Interstellar Missions		Long Calendar life	Li-Solid State?

Why Solid Electrolytes – NASA Relevance

- Li-ion electrolytes are combustible and pose serious safety issues.
  - Batteries require complex thermal and electrical management and mechanical reinforcement.
  - Non-flammable electrolytes haven't come to fruition yet
  - Solid electrolytes are expectedly more stable electrochemically stable towards Li, and have wide electrochemical window but have low ionic conductivity
- High specific energy with Li metal anode
- Excellent Cycle life (>10,000 cycles) and calendar life >15 years for deep-space missions
- Wide temperature range for NASA missions
  - No sharp drop in conductivity at low temperature unlike liquid electrolyte
  - Stable at high temperatures up to 150C for Venus applications
  - Amenable to heat-sterilization (for planetary protection)
- Recent solid electrolytes have comparable conductivity (1 mS/cm at RT)

Are solid state Li cells good for low temperature operations?



From Eric Watchman's paper

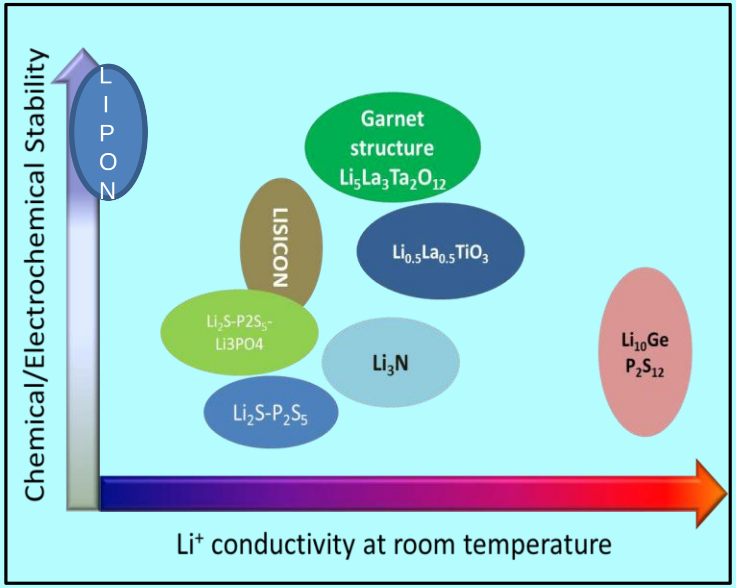
Li^+ Solid Electrolytes

- New types of solid electrolytes with high Li conductivity comparable to liquid electrolytes:

Electrolyte	Li^+- ion Conductivity	Remarks
Lithium Aluminum Titanium Phosphate (Ohara)	(10^{-4} S/cm)	High ionic conductivity, Poor stability towards Li , needs an interfacial layer. Thermally stable up to 600°C. Stable in water and no through-hole penetration, Li-air and Li-seawater batteries
Lithium Lanthanum Zirconium Oxide-LLZO	(10^{-4} S/cm)	High ionic conductivity, Good high voltage stability, Questionable stability towards Li anode, needs an interfacial layer
Lithium Germanium Phosphorous Sulfide (LGPS)	(10^{-3} S/cm)	High ionic conductivity, Not stable towards high voltage cathodes, Questionable stability towards Li anode,
Lithium Phosphorous Sulfur Chloride (Li_6PS_5Cl)	(10^{-3} S/cm)	
Lithium Phosphorous Oxynitride (LiPON)	(10^{-6} S/cm)	Low conductivity, Excellent stability towards Li anode, senstive to moisture, Free-standing membrane not possible,

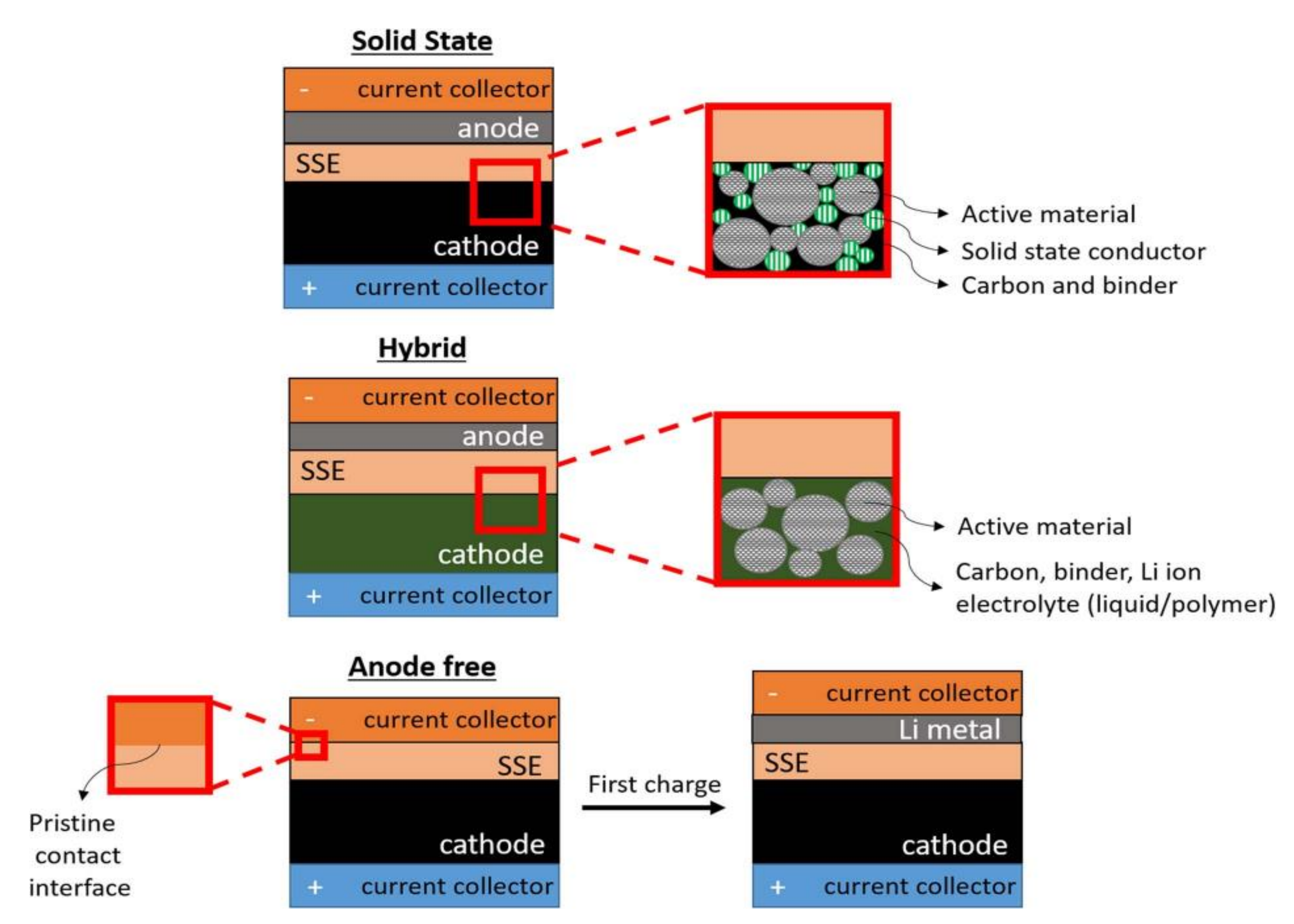
- Sodium ion conductor
  - B" alumina 10^1 S/cm at >250C

- Ionic Conductivity: LGPS > LPSCl > LLZO > LATP > LiPON



From Goodenough's paper

Solid Electrolyte Cell Designs



K. Kerman, A. Luntz, V. Viswanathan, Y. M. Chiang and Chena, Journal of The Electrochemical Society, ***164*** *(7) A1731-A1744 (2017)*

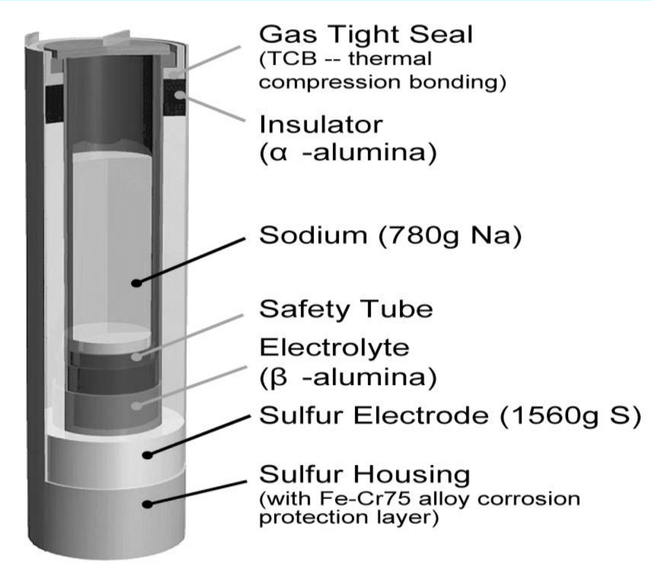
Challenges with the Solid Electrolytes

- Fabricating thin (dense) electrolyte pellets/membranes
  - Dispersion in polymer electrolytes
- Getting good interface across solid electrode and solid electrolyte
- Electrochemical stability towards Li (and high voltage cathodes)
- Composite cathodes
  - High aerial capacity (4 mAh/cm^2)
  - Dispersion of solid electrolyte in the cathodes (higher amounts of electrolyte lowers specific energy)
  - Dense cathode to allow Li ion penetration
  - High power densities
- Alternately, hybrid cells with solid electrolyte (on Li) in conjunction with liquid electrolyte

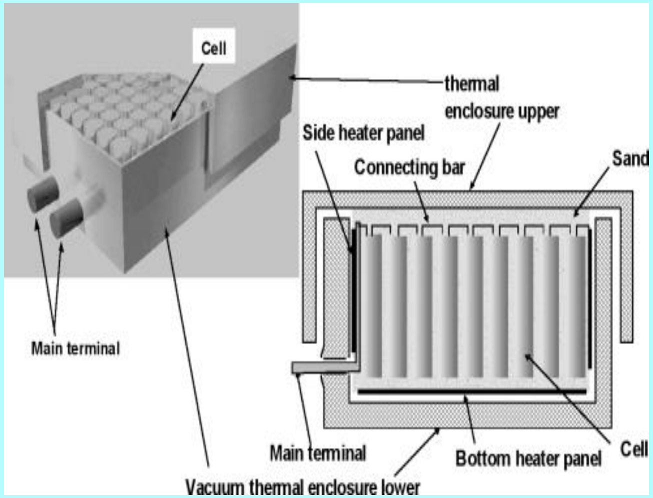
Sodium-Sulfur Batteries (Na-S)

- Chemistry
  - Uses (molten) sodium as the anode and (molten) sulfur as the cathode, and sodium-ion-conductive β-alumina ceramic as the electrolyte/separator.
  - Operate at ~300-350°C
- Cell Reaction: 2Na + xS = Na_2S_x 2.08 V
  Charge Discharge
- Performance
  - High specific energy (150 Wh/kg)
  - 100% coulombic efficiency, i.e. no self- discharge.
  - Excellent cycle life: 40,000+ cycles to 20%, 4500 cycles to 90%, and 2500 cycles to 100% depth of discharge.
- Status
  - Currently used in stationary applications 1.5 to 35MW manufacturers: NGK Insulators (Japan); Ford aerospace (past)
- Issues
  - Reliability and safety issues emanating from the failure of the brittle ceramic separator (beta alumina).

Sodium-Sulfur Cell



Sodium-Sulfur Battery

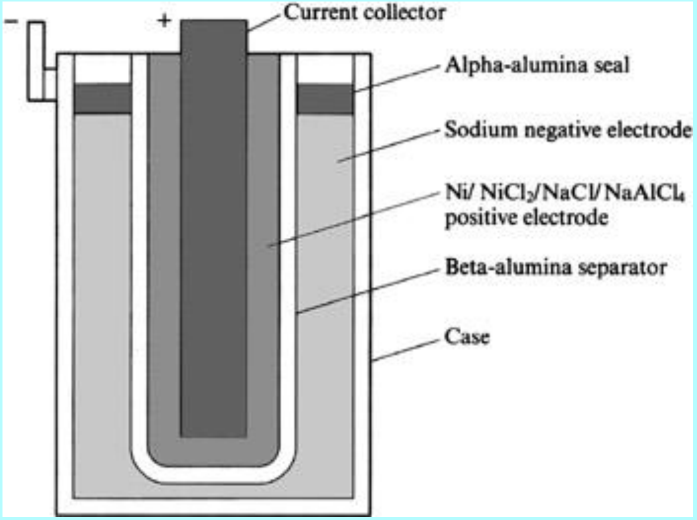


Sodium-Metal Chloride Batteries (Na-MCl_2)

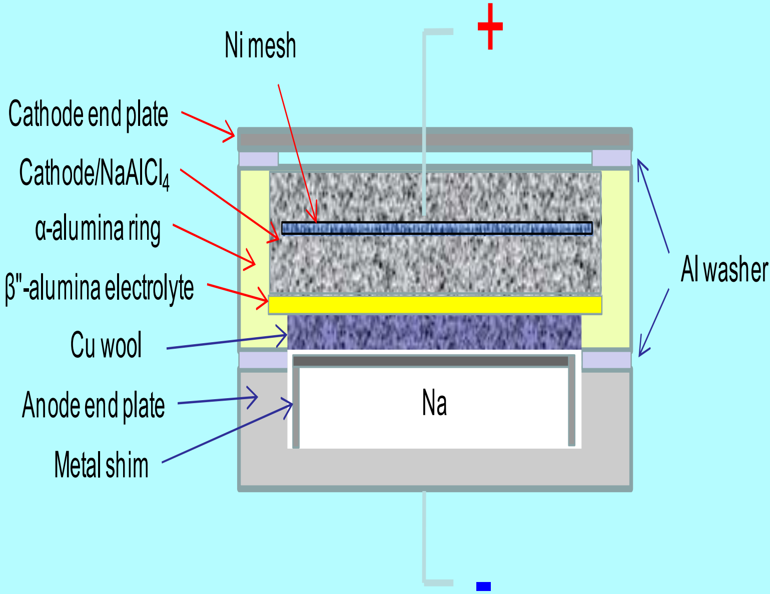
- Chemistry
  - Uses (molten) sodium as the anode and solid metal chloride (iron or nickel) as cathode in sodium tetrachloro-aluminate melt and with Na^+-ion-conductive β-alumina ceramic as the separator electrolyte.
  - Operate at ~300-400°C
- Cell Reaction: $NiCl_2 + 2Na = 2NaCl + Ni$ 2.6 V

  Charge Discharge
- Performance
  - Specific energy: 115 Wh/kg; Energy density: 160 Wh/L
  - Cycle Life: > 2000 cycles at 100% DOD and >3,000 cycles at 80% DOD.
  - Safer and more reliable than Na-S
- Status
  - Currently used in stationary and vehicular applications 1.5 to 35MW manufacturers: FIAMM Sonick and General Electric, Eagle Picher and PNNL
- Issues
  - Reliability and safety emanating from the failure of the ceramic separator (beta alumina).

Sodium- Nickel Chloride Cell

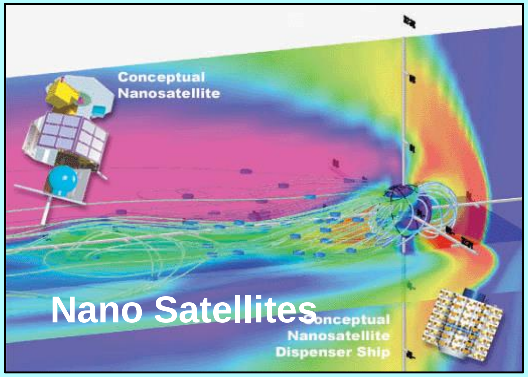


Planar Sodium- Nickel Chloride Cell

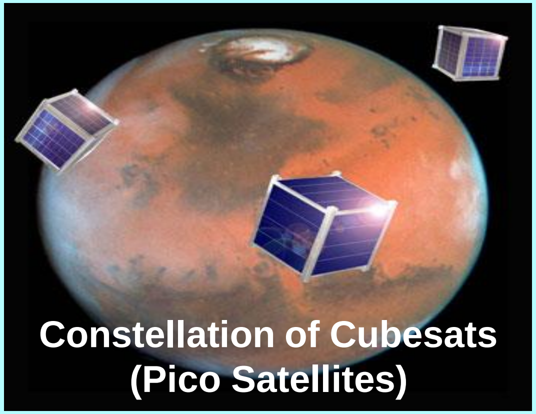


Solid State Microbatteries

- Need for very low power, low profile and low mass micropower sources for micro/nanospacecraft applications based on the recent successes in the effort to miniaturize spacecraft components using MEMS technology, integrated passive components, and low power electronics
- The miniaturization and integration of power sources with the devices to be powered will enable the concept of distributed sensing for a host of planetary wide-area sampling and exploration missions.
- Co-locating microscale batteries and integrated circuits on the same chip (System on A Chip).



Study Earth's magnetotail with a constellation of 50-100 "nano-spacecraft" (20 kg total mass), Mass<10Kg; Power ≈ 10W and a Rechargeable battery



Spacecraft architecture based on the Stanford Cubesat bus (4' x 4" x 4", 1 kg total mass).
Mass< 1Kg; Power≅ 1W
Battery: Rechargeable

LIPON Electrolyte (ORNL)

- Lithium phosphorous oxynitride by sputtering Li_3PO_4 in N_2
- Single Li^+ conducting phase with a conductivity of 2.3 x 10^{-6} at 25°C
- No detectable reaction or degradation at the Li/LiPON interface
- Wide electrochemical window of 0-5.5 V

Arrhenius plot of LiPON conductivity

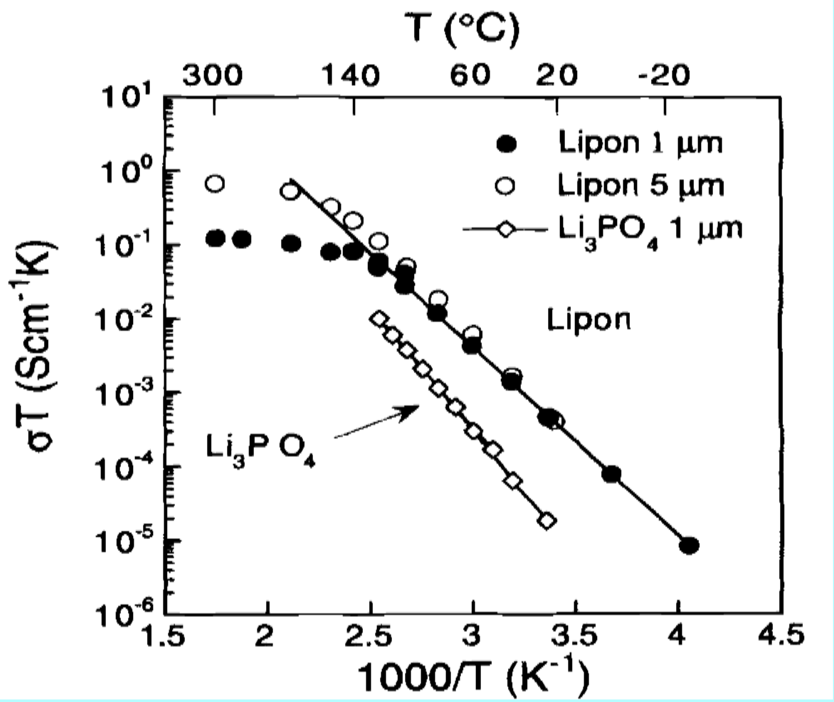


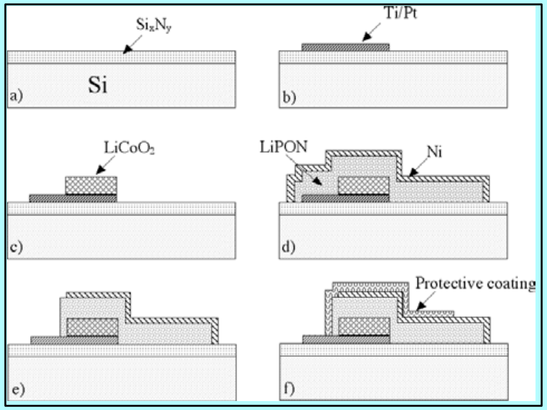
Table I. Compositions, Li^+ ion conductivities, and activation energies for films deposited by sputtering Li_3PO_4 in Ar + O_2, Ar + N_2, and N_2.

Process gas composition	Li/P (PIGE)	Film composition[a]	Atom percent, N	$\sigma(25°C) \times 10^8$ (S/cm)	E_a (eV)
Ar + 20% O_2	2.8	$Li_{2.7}PO_{3.9}$	0	7	0.67
Ar + 7% N_2	3.1	—	—	39	0.64
Ar + 20% N_2	3.4	—	—	84	0.60
N_2	3.1	$Li_{3.1}PO_{3.8}N_{0.16}$	2	200	0.57
N_2	3.3	$Li_{3.3}PO_{3.8}N_{0.22}$	3	240	0.56
N_2	2.9	$Li_{2.9}PO_{3.3}N_{0.46}$	6	330	0.54

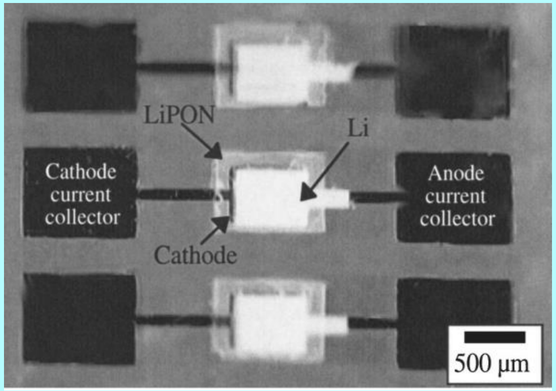
Xiaohua Yu, J. B. Bates G. E. Jellison, Jr., and F. X Hart, J. Electrochem. Soc, 122, 524 (1997)

Lithium Microbatteries (at JPL)

- Based on ORNL thin-film battery design
  - Consists of a RF (radio frequency) magnetron sputtered Co adhesion film, Pt cathode current collector,
  - $LiCoO_2$ cathode,
  - $Li_{3.3}PO_{3.8}N_{0.22}$ solid electrolyte(500-2000 nm) prepared by RF magnetron sputtering Li_3PO_4 in N2,
  - and either a thermally evaporated Li anode or a sputtered Ni or Cu blocking anode film that serves as a substrate for *in situ* Li plating during charging.
- Photolithography was carried out using a Solitec 3000 mask aligner.
- Cathode film annealed at 300ºC (vs 700ºC for ORNL) to be amendable to back-end Si processing (lower rate capability, however). Annealing decreases the $LiCoO_2$ lattice strain and increase grain size
- Parylene protective coating



Schematic Process flow for microfabricated batteries



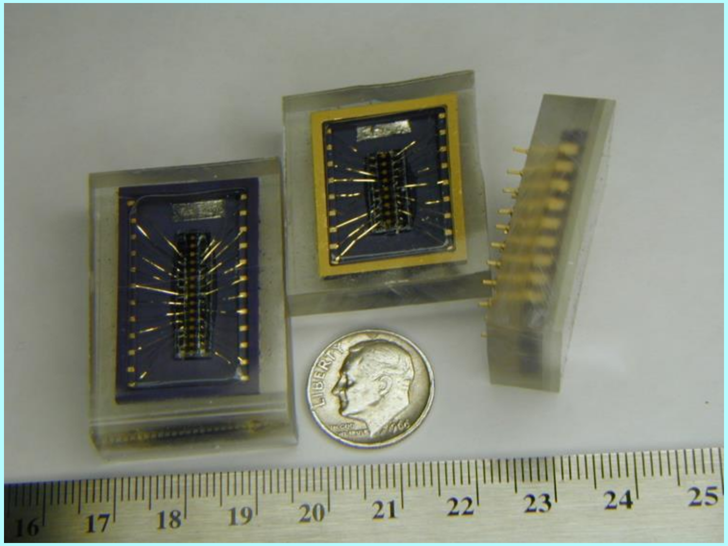
Optical micrograph of a fully microfabricated thin-film test cell

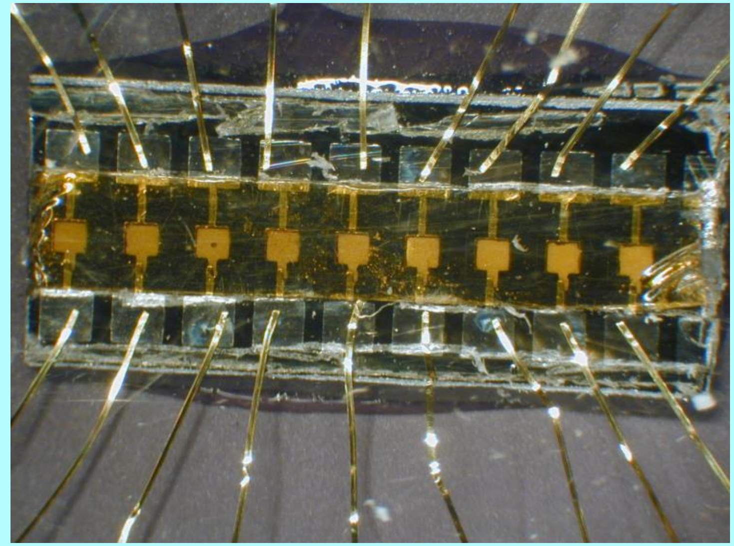
Table 1. RF magnetron sputter deposition conditions.

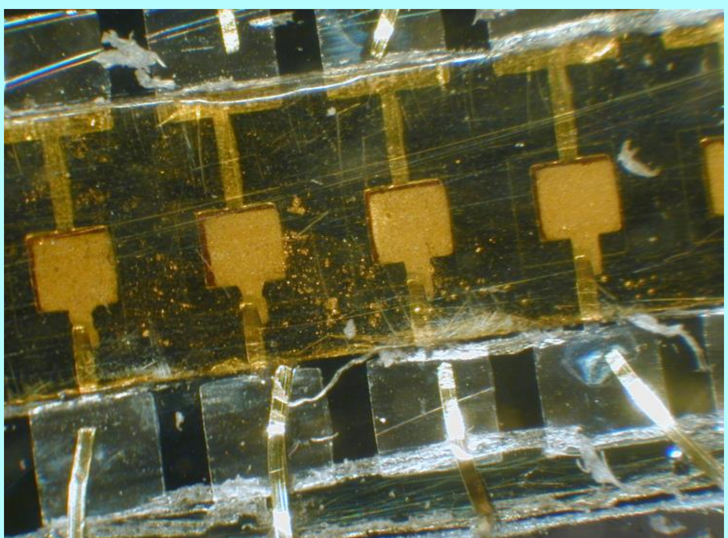
Film	Target	Sputter target power density ($W\ cm^{-2}$)	Sputter gas	Deposition pressure (mTorr)	Nominal thickness (nm)
Ti	Ti	6.6	Ar	10	10
Pt	Pt	6.6	Ar	10	200
$LiCoO_2$	$LiCoO_2$	2.2	25% O_2 75% Ar	10	250
LiPON	Li_3PO_4	2.2	N_2	15	500–2000
Ni	Ni	5.5	Ar	10	150

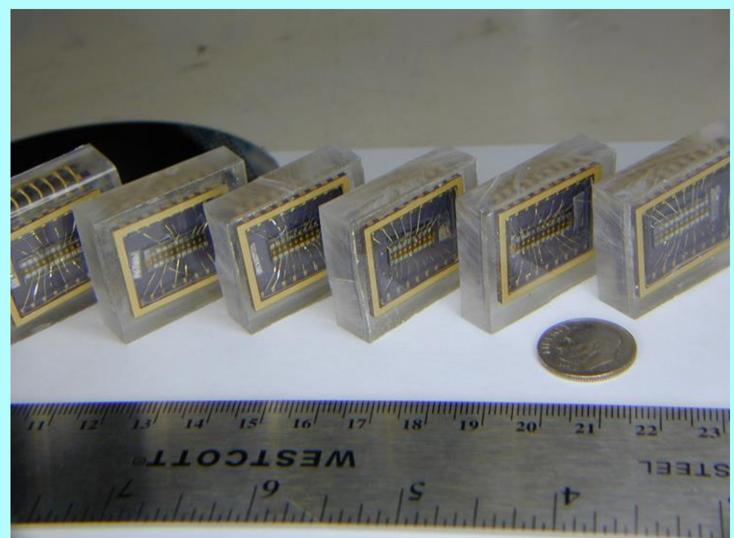
W C West, J F Whitacre, V White and B V Ratnakumar, J. Micromech. Microeng. 12 (2002) 58–62

Demonstration of Robust Packaged Microbatteries



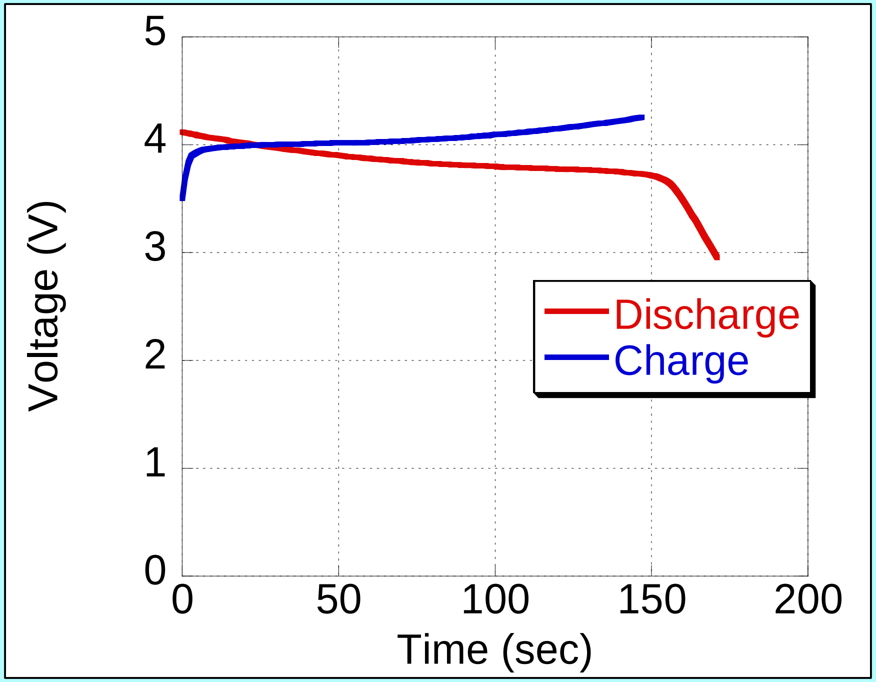


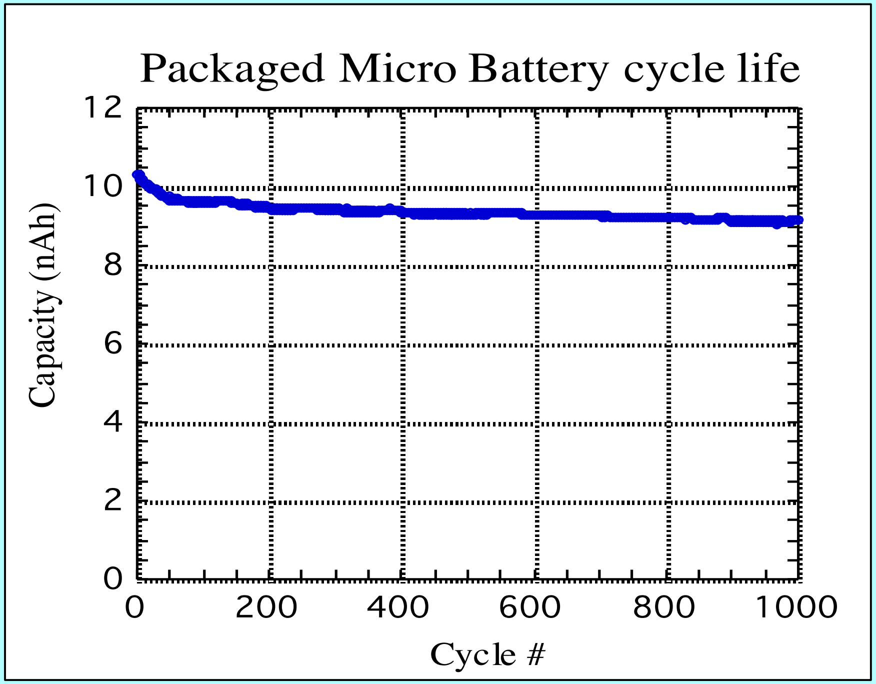




Microbattery Cell Performance

- Cells made with Li anode and optimized fabrication process



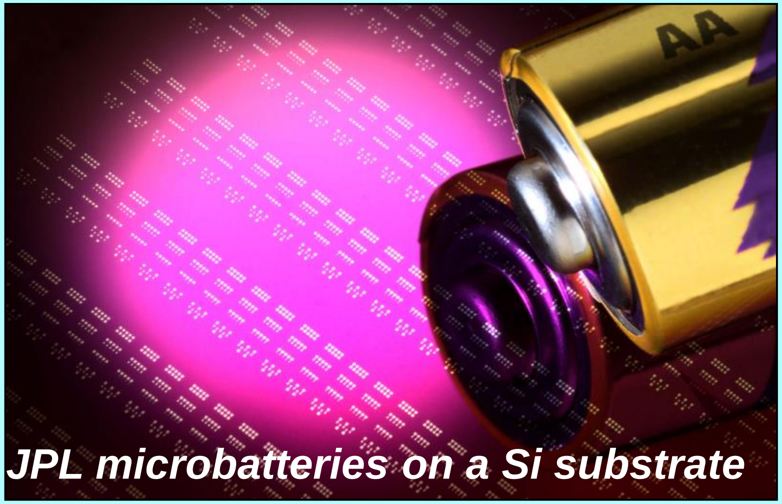


- ~3.8 V Discharge plateau,
- Excellent coulombic efficiency

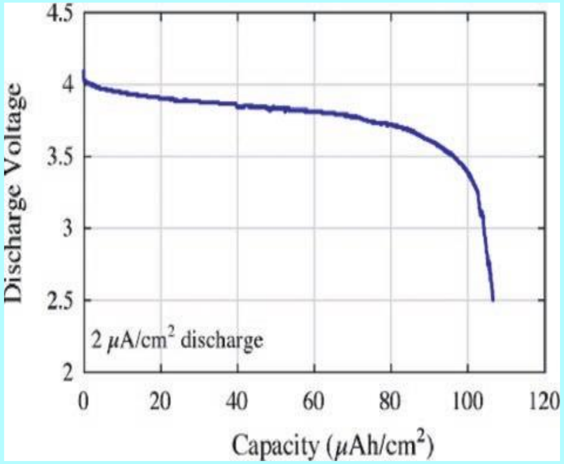
- > 1000 cycles with minimal capacity fade

Microbatteries for low power high voltage applications

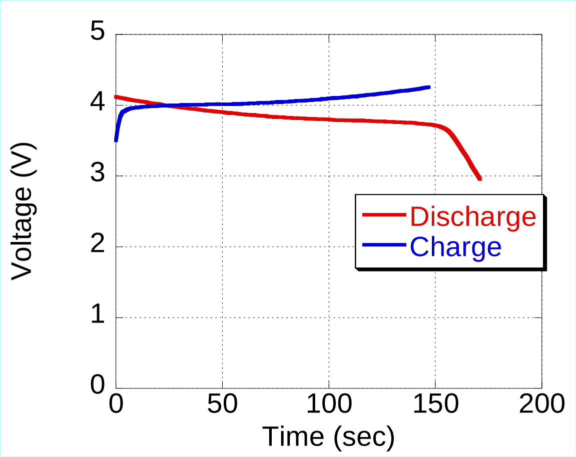
- Approximately 20,000 individual microbattery cells per 4″ Si wafer with footprints (50-100 mm)^2 are routinely fabricated in roughly 6 h of processing time.
- 10 μA h cm^{-2} capacity for a 0.25 μm cathode film at a 10 μA cm^{-2}
- Approximately 30,000 micro-batteries can be arranged on a wafer the size of a CD-ROM, at current packing density.
- Cells may be arranged in series or parallel, yielding a wide range of available voltages and capacities.
- Provides local “point of use” power to enable microsensors to operate autonomously.



JPL microbatteries on a Si substrate



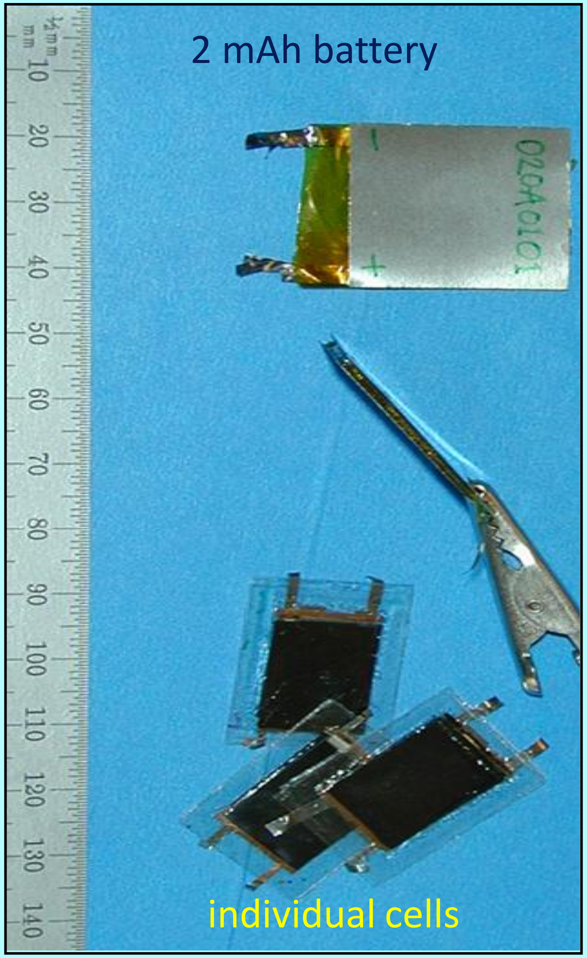
Discharge curve on optimized macroscopic thin film battery

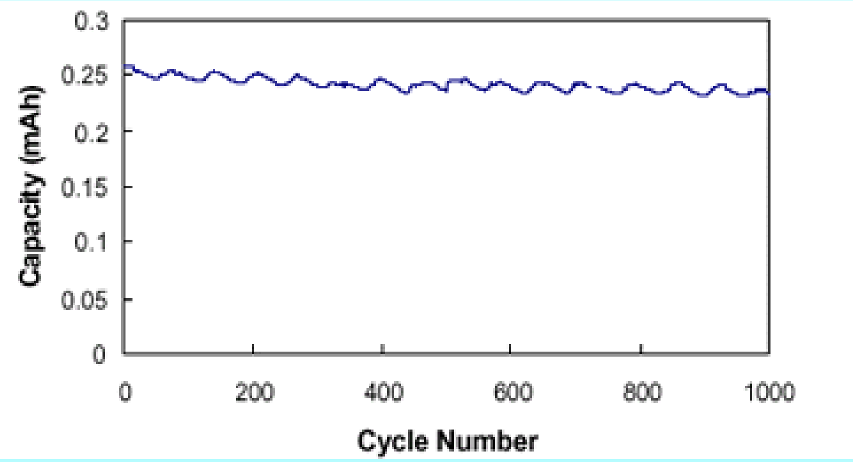


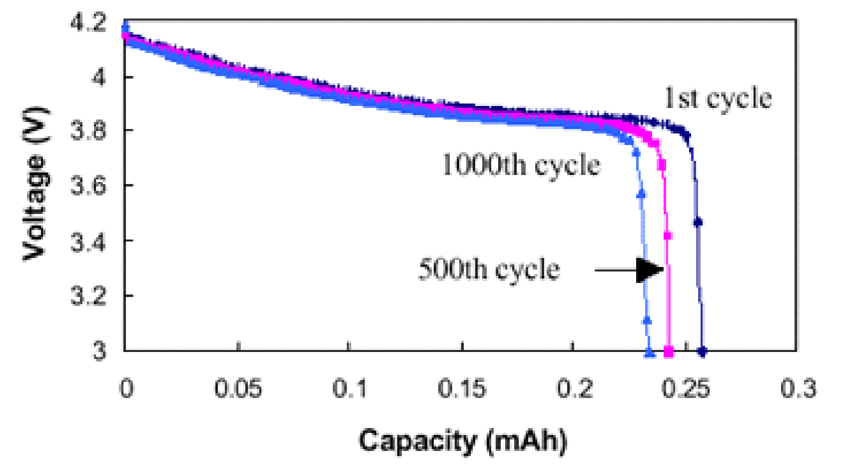
High rate charge and discharge profile for JPL microbatteries

W C West, J F Whitacre, V White and B V Ratnakumar, J. Micromech. Microeng. 12 (2002) 58–62

Multi-layer thin film solid-state battery





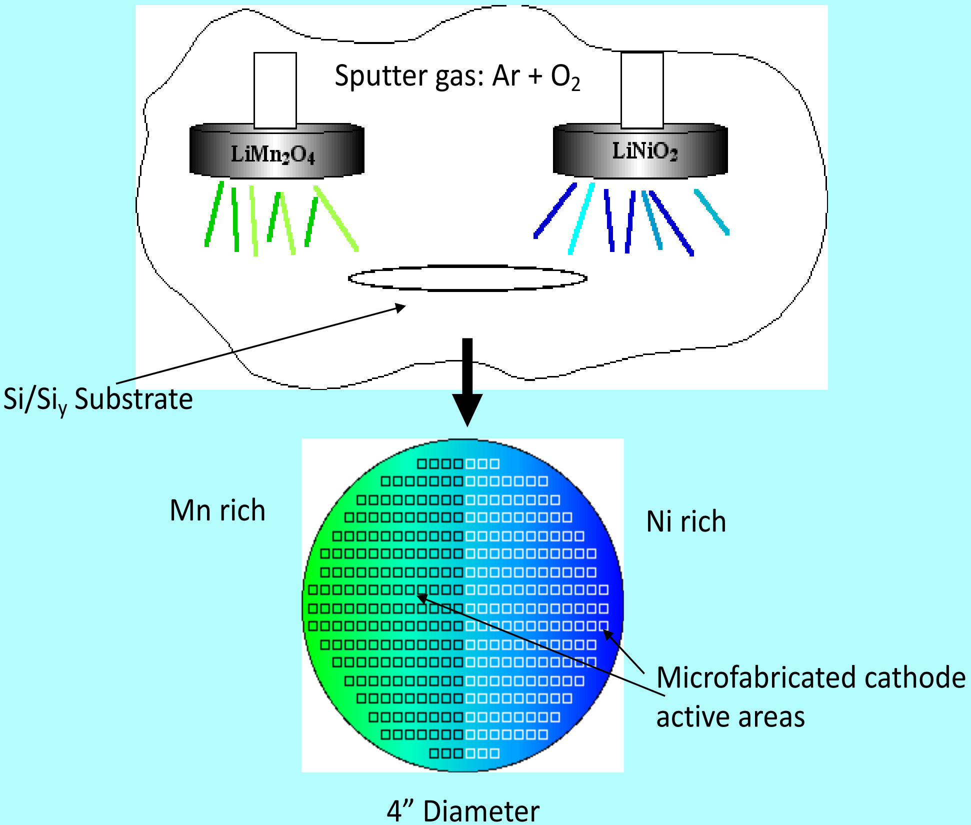


- Up to 8 mAh batteries created
- Excellent cycle life/rate capability In collaboration with industrial partner Front Edge Technology Excellent cycle life/rate capability
- Stainless/epoxy enclosure, Fully hermetic over at least 6 months

Solid State Cells for Cathode Combinatorial Study

- Thin-Film, Solid-State approach RF sputter-deposit from two different targets onto confocally oriented substrate.
- Composition varies continuously across substrate surface
- Fabricate LiPON-electrolyte Li-anode micro-batteries across wafer
  - Inorganic electrolyte/Li anode simple, minimize interface effects
- Relate cell location on substrate to composition/structure
- Evaluate performance electrochemically
- Spinel $LiMn_xNi_{2-x}O_4$

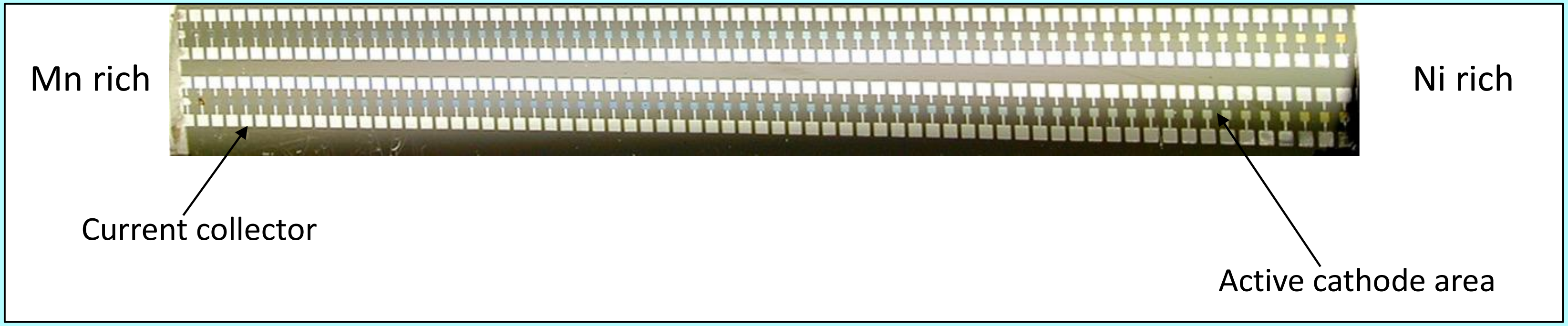
Cathode Layer Fabrication



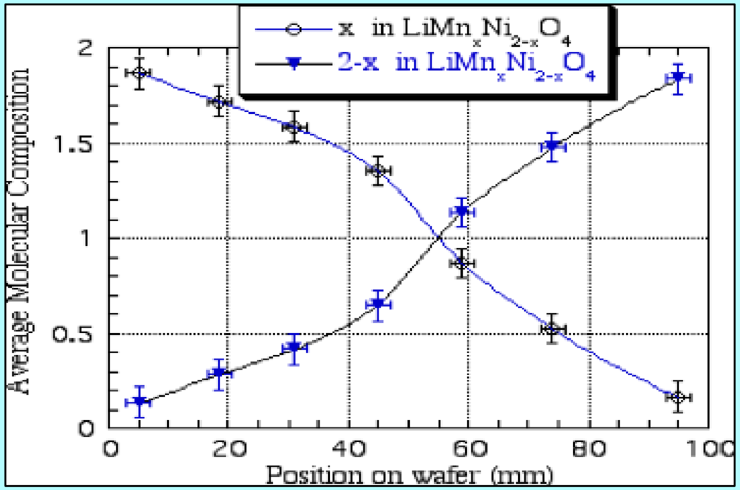
Solid State Cells for Cathode Combinatorial Study

$LiMn_xNi_{2-x}O_y$ Deposition

Pt Current collectors + cathode layers

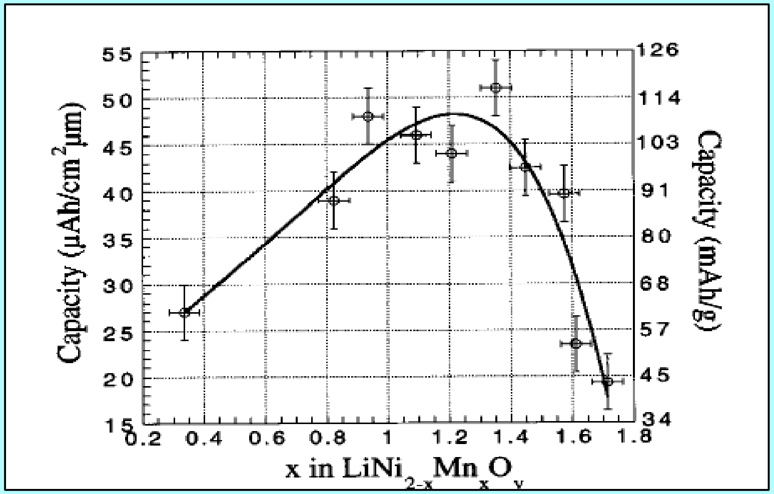


Compositional Variation



- From 80% Mn to 80% Ni

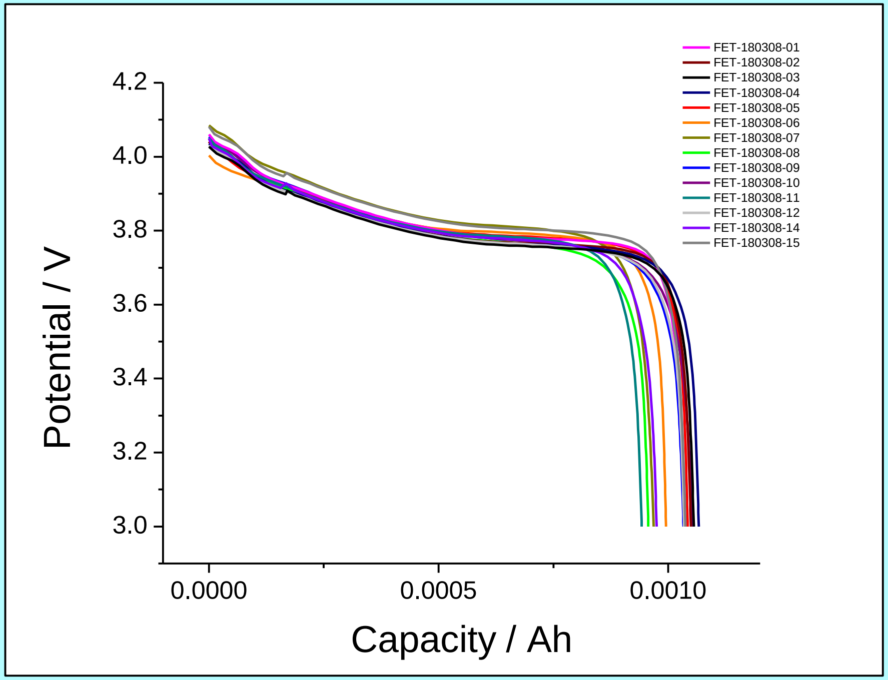
Capacity



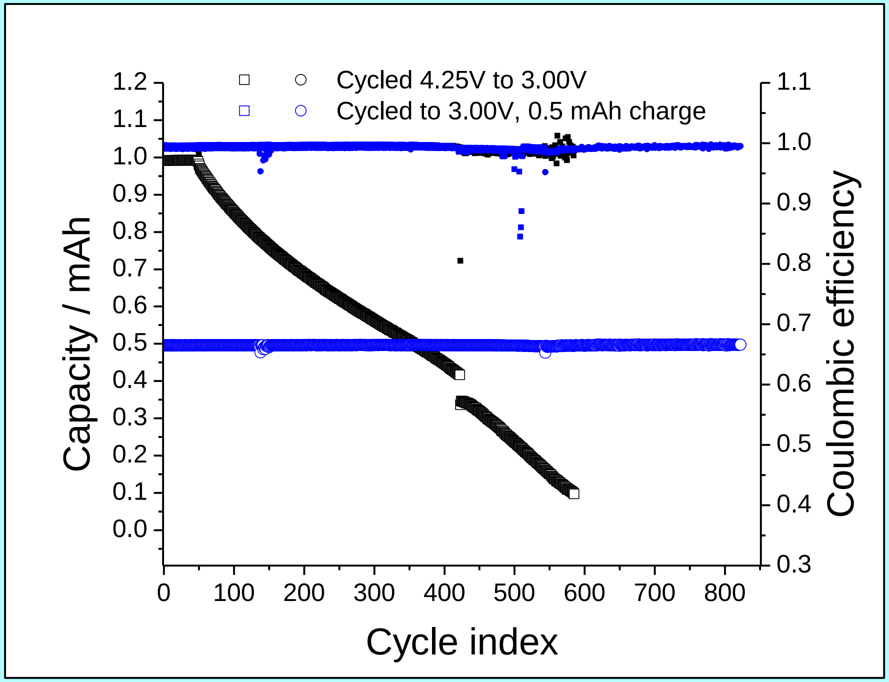
Cathode capacity ~by both volume and weight *vs.* composition.

J. Whtacre, W. West & B.V. Ratnakumar, J. Electrochem. Soc., **150,** A1676 (2003)

Lithium (Solid Electrolyte)Thin-film Cells



Discharge curve for 15 cells showing capacity spread (*C*-rate)



Cycling at 85 ºC at 100% and 50% DOD (bottom of charge curve) *C*-rate

- Cells held at 85ºC and 100% SOC show ~20% capacity loss after 6 months
- Cells held at 50% SOC show less than 10% capacity loss under same conditions

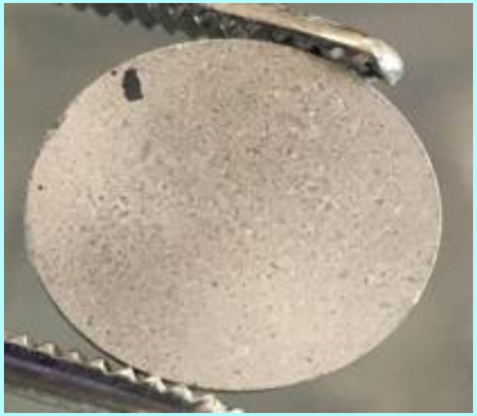
Electrolyte Systems under Evaluation

- LLZO (Lithium Lanthanum Zirconium Oxide) solid electrolyte pellets Univ. Of Michigan (Sakamoto's group)
- New solid electrolyte samples and dispersion fluids from NEI Corporation
  - Lithium Phosphorous Sulfur Chloride (Li_6PS_5Cl) powder
  - Lithium Germanium Phosphorous Sulfide (LGPS)
  - Lithium lanthanum zirconium oxide (LLZO)
  - H-polymer (with salt) powder
  - Solid Electrolyte dispersion fluid (H-polymer)

Electrolyte Systems under Evaluation

- Fabricated Thin Electrolyte Membranes
  - Coated Li with the polymer electrolyte using spin-coating’
  - Fabricated electrolyte pellets
  - Impregnated the standard Celgard (PE) separator
- Fabricated swage-lock and coin cells for assessing the solid electrolytes for the following characteristics:
  - Ionic conductivity from Electrochemical Impedance Spectroscopy
  - Stability with lithium assessed from cycling of Li/Li half cells

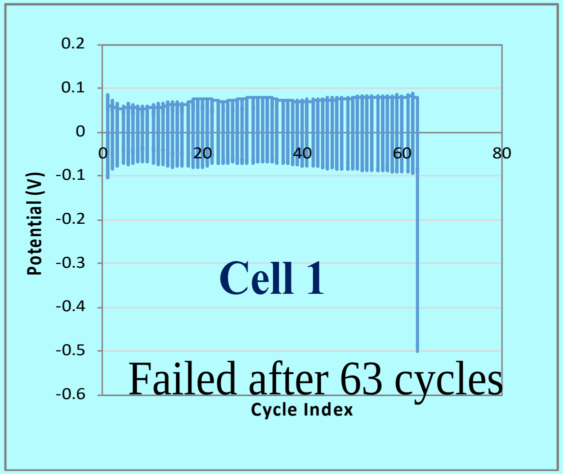
Solid electrolyte coated on Li (spin-coating)

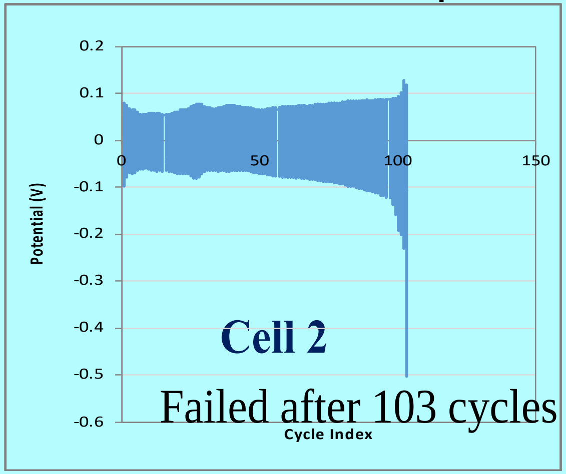


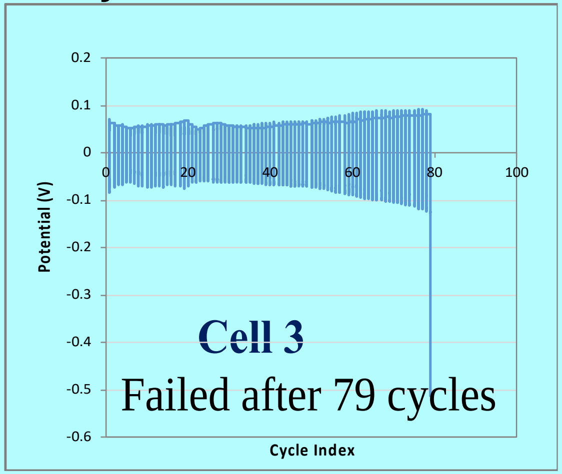
Thin solid electrolyte pellet (pellet) made by cold pressing

Baseline (Liquid) Electrolyte

Baseline Li/Li cells with liquid Electrolytes

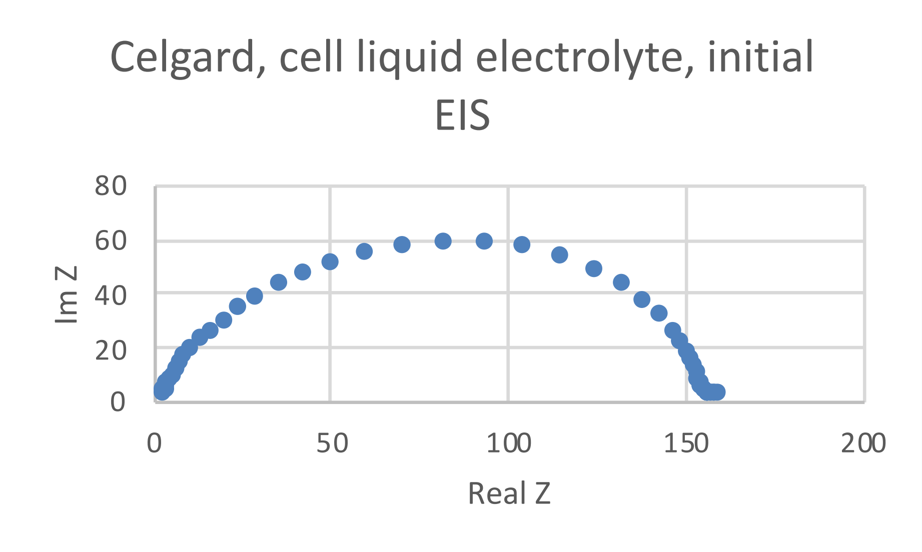




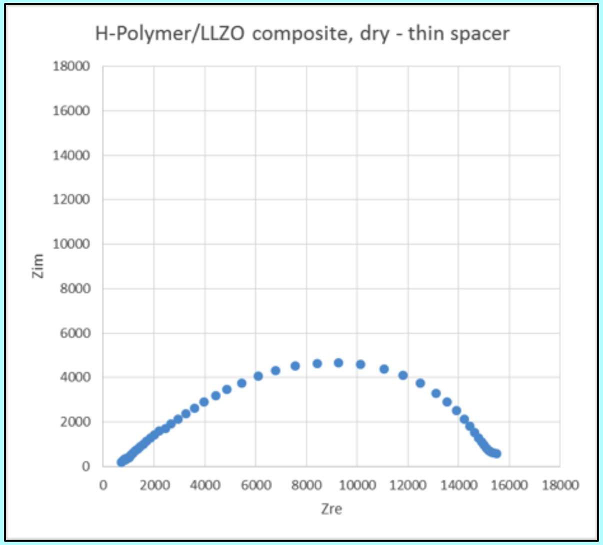


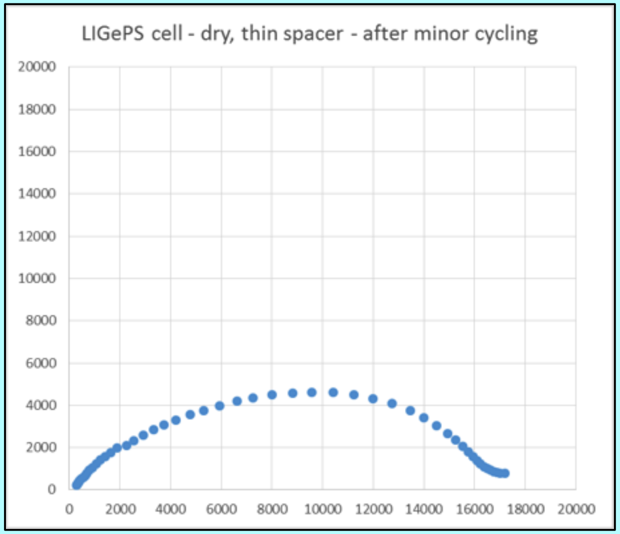
- Performance of Li/Li half cells during cycling at 8mA for one hour after conditioning, i.e., 5 cycles at 2 mA for 2 h, 4 mA for one hour and 8 mA for 0.5 h.

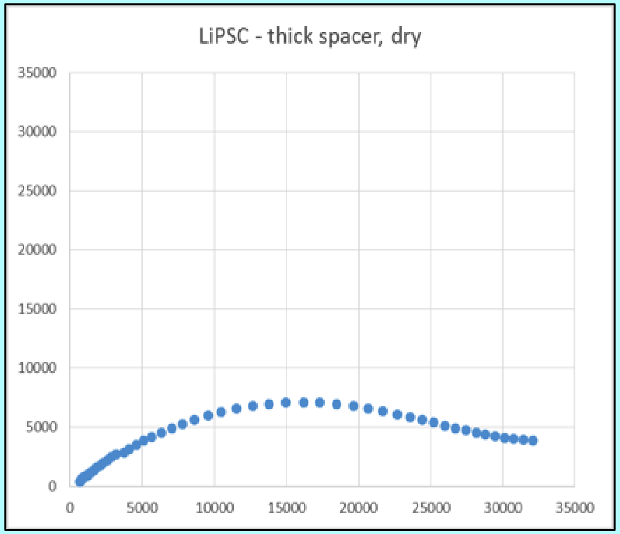
Baseline Celgard cell - cycling		
	High Freq	Low Freq
Initial	3.9	159
7 days	17.8	522
14 days	41.4	112
Baseline Celgard cell - no cycling		
	High Freq	Low Freq
Initial	3.4	157
7 days	7.1	393
14 days	8.2	439



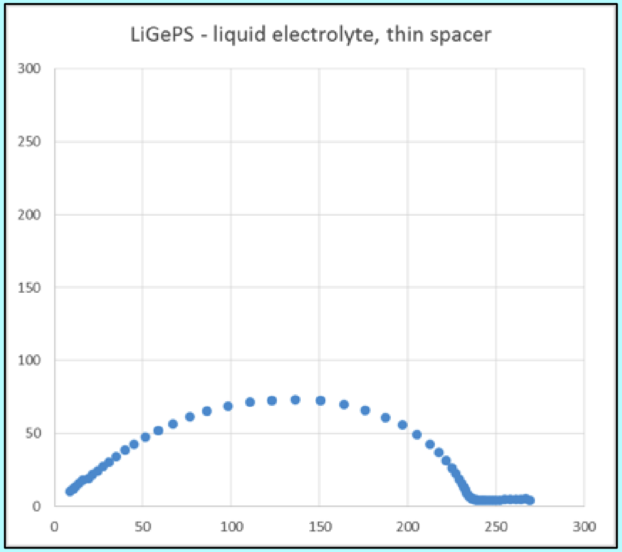
EIS of Li/SSE/Li

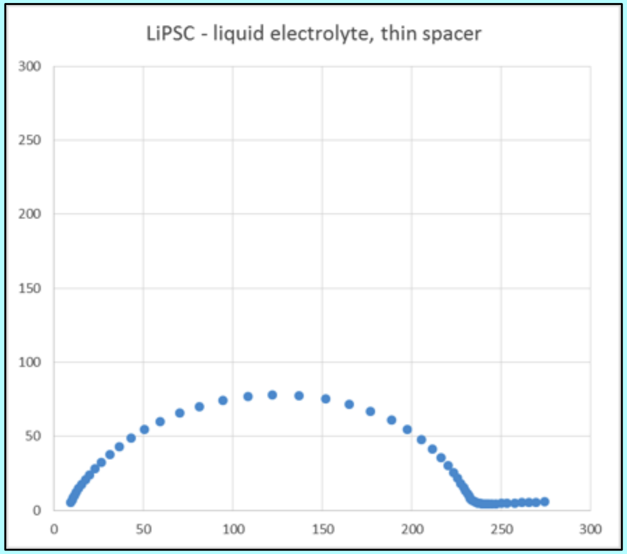




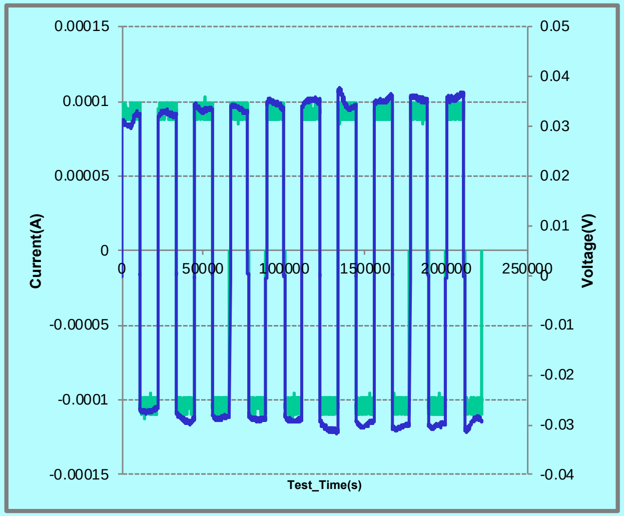


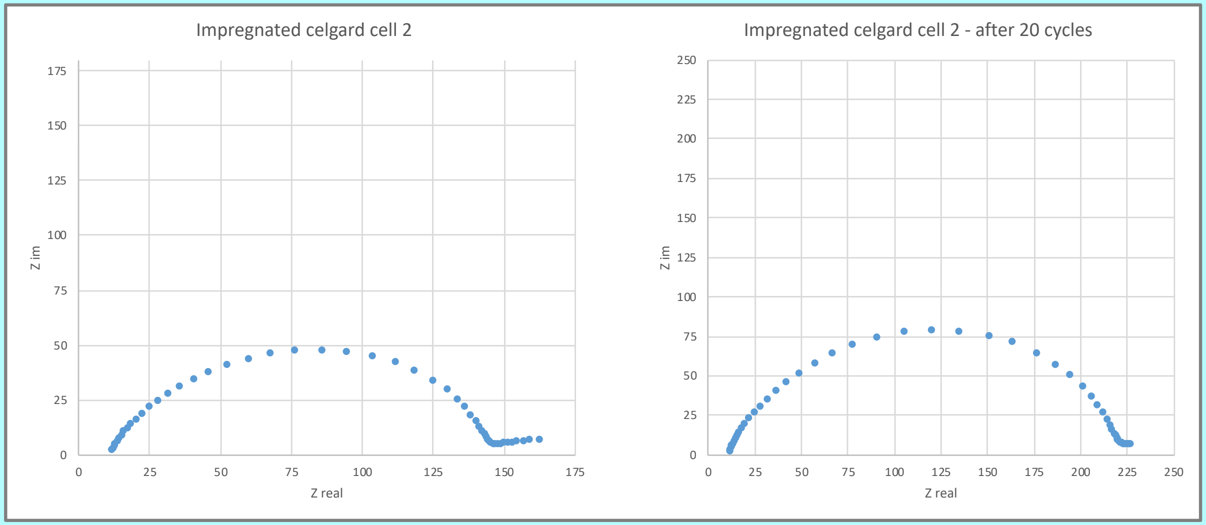
With two drops of liquid electrolyte





LLZO - Impregnated Celgard





- Ionic conductivity (series resistance) same as the baseline
- Marginal impedance growth upon cycling, from the reaction of Li with electrolyte

Summary

- NASA's future missions require energy storage devices with improved specific energy and energy density, long calendar life, cycle life.
  - Lithium solid state batteries are promising to provide enhanced specific energy by virtue of Li metal as the anode and also improved safety
  - Recent solid electrolytes have comparable ionic conductivity to conventional liquid electrolytes. However, many of these electrolyte do not have the required stability towards Li metal anode and warrant an interfacial layer.
  - It is a challenge to fabricate thin and dense membranes with these solid electrolytes. Use of polymer (ionically conducting) dispersions may be a viable approach.
  - Design of an efficient composite cathode with solid electrolyte blend is also a challenge to achieve high ionic conductivity and thus high (discharge) power densities.
  - LiPON is an excellent option for microbatteires with low area-specific capacity, with good cycle and calendar life. Microbatteries based on LiPON will be useful for sensor and 'System on A Chip' (SOAC) applications.
  - Development is underway globally to overcome the shortcomings of solid electrolytes for lithium rechargeable cells and to realize the potential of these materials for enhanced specific energy, safety and life.

Acknowledgements

This research was carried out at the Jet Propulsion Laboratory (JPL), California Institute of Technology under a contract with the National Aeronautics and Space Administration and supported by Center for Integrated Space Microsystems (CISM) and other internal R&D projects.